

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
24 October 2002 (24.10.2002)

PCT

(10) International Publication Number
WO 02/083621 A1(51) International Patent Classification⁷: C07C 69/76,
69/78, C08K 5/103, C08L 27/06Thomas; 100 Meaderboror Road, Rochester, NH 03867
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(21) International Application Number: PCT/US02/10907

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(22) International Filing Date: 4 April 2002 (04.04.2002)

(25) Filing Language: English

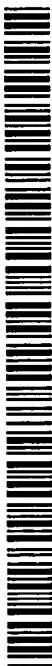
(81) Designated States (*national*): AT, AU, BR, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, IN, JP, KR, LU, MX, NO, NZ, PH, PL, PT, RU, SE, SG, VN, ZA.(30) Priority Data:
09/832,554 11 April 2001 (11.04.2001) US(84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

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Published:
— with international search report

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

**WO 02/083621 A1**

(54) Title: BENZOATE/ALKANOATE ESTER COMPOSITIONS

(57) Abstract: Mixtures of esters produced by reacting an aromatic and an aliphatic monocarboxylic acid with a stoichiometric quantity of a diol are effective plasticizers for polyvinyl chloride and other rigid organic polymers. The freezing point of the mixtures and the efficacy of the present ester mixtures as plasticizers can be varied by adjusting the type and molar ratio of the two types of acids used to prepare the ester mixture.

BENZOATE/ALKANOATE ESTER COMPOSITIONS

5

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to novel ester compositions. More particularly, this invention relates to mixtures comprising 1) the diester of a diol containing from 2 to 6 carbon atoms and benzoic acid or a substituted benzoic acid, 2) a mixed ester of said diol, said acid and an aliphatic monocarboxylic acid and, 3) a diester of said diol and said aliphatic monocarboxylic acid. Small concentrations of the monoester of 1) said diol and 2) said aromatic and/or aliphatic carboxylic acids can also be present.

Preferred ester compositions of this invention are low viscosity liquids at 25° C, are considerably less volatile and lower melting than the corresponding benzoic acid diesters, and are effective primary plasticizers for rigid halogen-containing organic polymers such as polyvinyl chloride.

20 The Prior Art

Many esters of organic acids are known to be useful plasticizers for a variety of organic polymers. Esters of 1) monohydric alcohols and phthalic acid and 2) mono- or dihydric alcohols and benzoic acid are particularly preferred plasticizers for vinyl chloride homopolymers and copolymers based on their cost and performance.

25

While esters of mono- or dihydric alcohols and aliphatic monocarboxylic acids containing eight or more carbon atoms lower the viscosity and impart low temperature flexibility to vinyl chloride polymers, the incompatibility of the aliphatic acid esters with these polymers limits

their utility to secondary plasticizers in combination with benzoic or phthalic acid esters as the primary plasticizer. A disadvantage of this approach is that the plasticizers selected may not be compatible with one another and /or with the vinyl chloride or other polymer to which the ester mixture will be added as a plasticizer.

5

A second approach to combining the advantages of aliphatic and aromatic acids as plasticizers is to prepare a mixed ester. This can be done by first forming a half ester by reacting a dihydric alcohol, hereinafter referred to as a diol, with half a molar equivalent of one of the monocarboxylic acids or a suitable derivative thereof, such as the corresponding acid halide.

10 The resultant half ester is then isolated and reacted with the other acid or a derivative thereof. The final ester can be represented by the generic formula R'C(O)OR(O)CR'', where R represents the hydrocarbon portion of a diol, R' represents the hydrocarbon portion of the aromatic monocarboxylic acid and R'' the hydrocarbon portion of the aliphatic monocarboxylic acid.

15

The performance as plasticizers for polyvinyl chloride of benzoate/alkanoate mixed esters of the aliphatic diols ethylene glycol, diethylene glycol and 2-butene-1,4-diol is described by A.V. Bailey et al. in the Journal of the American Oil Chemists Society, 53 (5):176-8 (1976). The esters were obtained by first reacting the desired diol with benzoyl chloride and then reacting the resultant half ester with the acid chloride of desired aliphatic acid. These acids contained from 5 to 20 carbon atoms.

25 Bailey et al. report that the benzoate/laurate mixed ester of diethylene glycol exhibits an optimum combination of properties as a plasticizer, one of the reasons being that the other plasticizers evaluated were incompatible with polyvinyl chloride at concentration of 35 weight percent, based on the total weight of the polymer composition.

The mixed esters utilized by Bailey et al. are pure materials that require the two-stage preparation described in the preceding paragraphs using acid chlorides rather than the corresponding and relatively less expensive carboxylic acids.

5 The present invention is based on the discovery that useful, relatively inexpensive mixtures of aromatic and aliphatic acid esters can be prepared using a single step process. These ester compositions are useful primary plasticizers for homo- and copolymers of vinyl chloride and other rigid organic polymers.

10 In accordance with the present process a diol is reacted with a stoichiometric amount of a mixture of 1) benzoic acid or other aromatic monocarboxylic acid and 2) an aliphatic monocarboxylic acid. The molar ratio of the two carboxylic acids is adjusted to achieve the desired ratio of the two acid residues in the reaction product. The molar ratio of total acids to diol is typically 2:1.

15

The present ester compositions are considerably easier and less expensive to prepare than the pure aromatic/aliphatic mixed esters of the prior art and exhibit unexpectedly low levels of viscosity and volatility. Other advantages of the present ester compositions will be described in the present specification.

20

DETAILED DESCRIPTION OF THE INVENTION

This invention provides ester compositions comprising

I) an ester corresponding to formula (I)



25 2) an ester corresponding to formula (II)



3) an ester corresponding to formula (III)



wherein R¹ is at least one radical selected from the group consisting of phenyl and alkyl-substituted phenyl, R² is a divalent radical of the formula -R⁴(OR⁴)_m- , R³ is an alkyl radical containing from 3 to 21 carbon atoms , R⁴ is an alkyl radical containing from 2 to 4 carbon atoms, and m represents 0 or the integer 1 or 2.

5

The present ester compositions are prepared by reacting a diol of the formula HOR²OH with an aromatic monocarboxylic acid of the formula R¹C(O)OH and an aliphatic monocarboxylic acid of the formula R³C(O)OH, wherein the total moles of said aromatic and aliphatic carboxylic acids are equal to twice the number of moles of said diol and R¹, R² and R³ are as hereinbefore defined.

10

This invention also provides plasticized polymer compositions comprising 1) a homopolymer or copolymer of vinyl chloride and 2) a plasticizer comprising a mixed ester composition of the present invention.

15

In preferred embodiments of the present ester compositions, the molar ratio of R¹ C(O)- to R³ C(O)- groups in said composition is from 3:1 to 12:1, R¹ is phenyl, m is 1 or 2, and the composition is a liquid at 25° C.

20

The ester compositions of this invention can optionally contain up to about 5 percent by weight of monoesters of the diol HOR²OH and at least one of the aromatic and aliphatic carboxylic acids used to prepare the ester. These monoesters are represented in this specification by the formulae R¹C(O)OR²OH and R³C(O)OR²OH, wherein R¹, R² and R³ are as previously defined. The presence of these monoesters is typically not desirable because they increase the volatility of the ester composition.

25

To minimize the concentration of monoesters in the final ester mixture, the moles of aromatic and aliphatic acids used to prepare the esters should be equal to twice the number of moles of

diol. The concentration of monoesters can be further reduced by washing this mixture with an aqueous solution of a base such as potassium hydroxide.

An unexpected advantage of the present ester compositions is that by selecting preferred ranges for the molar ratio of the two monocarboxylic acids and the number of carbon atoms in the aliphatic carboxylic acid, the physical properties such as melting point, viscosity and volatility exhibited by the resultant mixture of esters and the compatibility of these mixtures with vinyl chloride polymers can be varied over a wide range to achieve a desired combination of properties. Preferred ester compositions and the molar ratio of aromatic to aliphatic carboxylic acids used to prepare them are described in subsequent sections of this specification.

Although the relative concentrations of the three possible diesters in a composition of the present invention is difficult to predict, because carboxylic acids typically react at different rates, the distribution of reaction products is influenced by the relative concentrations of aromatic and aliphatic carboxylic acids in the initial reaction mixture, the temperature of the reaction mixture and the total reaction time.

The accompanying examples demonstrate that a reaction mixture containing a 6:1 molar ratio of benzoic acid to the aliphatic carboxylic acid will produce an ester mixture containing a higher concentration of mono- and dibenzoates and a lower concentration of the mixed benzoate/alkanoate ester than a reaction mixture in which this molar ratio is 1:1. The inability to precisely predict the relative concentrations of the possible mono- and diesters in the present ester mixtures from the molar ratio of the two carboxylic acids used to prepare them does not affect the utility of the present mixtures as primary plasticizers for polyvinyl chloride and other rigid organic polymers.

Preparation of the Mixed Esters

The mixed ester compositions of this invention can be prepared by reacting the desired diol with a substantially equimolar quantity of a mixture consisting essentially of 1) an aromatic carboxylic acid selected from the group consisting of benzoic acid and substituted benzoic acids and 2) an aliphatic monocarboxylic acid containing from 3 to 21 carbon atoms.

Substituted benzoic acids such as toluic acid can be used in place of benzoic acid. It will be understood by those skilled in the art of ester preparation that derivatives of the aromatic and aliphatic carboxylic acids, such as the corresponding acyl halides and acid anhydrides, can be substituted for the acid.

10

While the molar ratio of the aromatic to the aliphatic carboxylic acid and the particular aromatic and aliphatic acids used to prepare the initial reaction mixture are not critical with respect to operability of the process used to prepare the present compositions, the molar ratio is preferably from 1 to 12 moles of the aromatic monocarboxylic acid per mole of the aliphatic monocarboxylic acid, the aromatic carboxylic acid is preferably benzoic acid and the aliphatic carboxylic acid preferably contains from 8 to 16 carbon atoms. These preferences are based on the properties, particularly melting point and volatility, of the resultant ester mixtures and the efficacy of the ester compositions as plasticizers for vinyl chloride polymers.

20 Diols suitable for use in preparing the ester compositions of the present invention can be represented by the general formula $\text{HOR}^4(\text{OR}^4)_m\text{OH}$. In this formula R^4 represents an alkyl radical containing from 2 to 4 carbon atoms, and m represents 0 or the integer 1 or 2.

25 Suitable diols include but are not limited to ethylene glycol, propylene glycol, 1,3-propanediol, 2-methyl-1,3-propanediol, diethylene glycol, dipropylene glycol, triethylene glycol, 1,3-butanediol and 1,4-butanediol. Diols wherein R^4 is ethyl or n-propyl and m is 1 or 2 are preferred based on their cost and commercial availability.

Because esterification is typically a reversible reaction, this reaction is typically conducted at the boiling point of the reaction mixture and the water produced as a by-product of the reaction is preferably distilled from the reaction mixture and collected. To increase the rate of the esterification reaction, it is preferably conducted in the presence of a suitable catalyst such as a mineral acid, an organotin compound, an organotitanium compound and/or a zirconium compound. Suitable catalysts include but are not limited to the organic sulfonic acids such as toluene sulfonic acid, tin compounds such as stannous octoate, tetrabutyl titanate and zirconium carbonate. These catalysts can be used alone or in combinations of two or more.

The procedures and equipment used to prepare, isolate and analyze the ester mixtures produced from the esterification reaction are sufficiently well known to those skilled in this art that a detailed discussion is not required as part of the present specification. Gas chromatography is a preferred method for determining the types and relative concentration of the esters in the present compositions.

15

When equal numbers of moles of diethylene glycol, benzoic acid and lauric acid were reacted and the resultant mixture of esters treated with aqueous potassium hydroxide solution followed by washings with water to reduce the concentration of monoesters, analysis of the product using gas chromatography showed the mixture to contain less than 0.5 percent diethylene glycol monobenzoate, 4 percent diethylene glycol monolaurate, 14 percent diethylene glycol dibenzoate, 45 percent diethylene glycol monobenzoate monolaurate and 36 percent diethylene glycol dilaurate, based on the relative areas of the peaks on the output chart of the chromatograph.

25 Properties of Preferred Mixed Esters

Ester mixtures prepared by reacting benzoic acid and a carboxylic acid containing from 9 to about

14 carbon atoms with one of the present diols are preferred based on their unexpected combination of properties that make these esters particularly useful primary plasticizers for organic polymers such as homopolymers and copolymers of vinyl chloride.

- 5 Data in the accompanying examples demonstrate that the viscosity and freezing point of these esters are unexpectedly low relative to the corresponding diester of benzoic acid. As the molar ratio of benzoic acid to lauric acid in the initial reaction mixture increases from 1:1 to 9:1 the freezing point of the resultant ester mixture decreases from 25° C to a eutectic point at about –15° C. As this ratio increases beyond 9:1 to the absence of the aliphatic carboxylic acid, the
10 freezing point of the resultant ester mixture increases to about 25° C for diethylene glycol dibenzoate.

Performance of the Present Mixed Esters as Plasticizers

- Mixed esters prepared from benzoic acid, an aliphatic carboxylic acid containing from 8 to 16
15 carbon atoms and a diol such as diethylene glycol are particularly useful plasticizers based on the unique and unexpected combination of an unexpectedly low freezing point and low volatility of the mixed ester and the low viscosity and relatively low gel temperature of the plasticized polymer. In addition to homo-and copolymers of vinyl chloride, other types of polymers suitable for use with the present ester compositions include but are not limited to
20 thermoplastic polymers such as cellulose ester polymers, polystyrene, and chloronated polyethylene, and elastomers such as polyacrylics, styrene/butadiene copolymers and natural rubber.

- The following examples describe preferred embodiments of the present ester mixtures, a preferred method for preparing them, the physical properties of these mixtures and the
25 properties of polyvinyl chloride compositions containing these mixtures as primary plasticizers. The examples should not be interpreted as limiting the scope of the invention defined in the accompanying claims. Unless otherwise specified all parts and percentages in

the examples are by weight and the physical properties of the esters mixtures were measured at 25° C.

EXAMPLE 1

5 Four mixed ester compositions of the present invention were prepared by charging a glass reactor with diethylene glycol ($\text{OHCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$) as the diol, benzoic acid as the aromatic carboxylic acid, lauric acid as the aliphatic carboxylic acid, and, as the catalyst for the esterification reaction, 0.1 percent, based on the weight of total reactants, of a catalyst mixture containing 75 weight percent zirconium carbonate and 25 weight percent stannous 10 oxalate. The molar ratio of benzoic to lauric acids present in the four initial reaction mixtures is listed in

Table 1. The molar ratio of total carboxylic acids to glycol was 2:1 in all of these reaction mixtures.

15 The reactor was equipped with a thermometer to measure the temperature of the reaction mixture, a mechanically driven stirrer, an inlet for nitrogen extending below the surface of the reaction mixture, and a trap to collect the water that distilled as a by-product of the esterification reaction. A water-cooled reflux condenser was located above the trap.

20 The contents of the reactor were gradually heated to liquify the solid reactants and initiate vaporization of volatile materials. At a reaction mixture temperature of about 180° C all of the initial reactants had liquified and vaporized liquid had begun to condense and collect in the trap. The boiling point of the reaction mixture gradually increased to 250° C. Following about 4 hours of heating the acid number of the reaction mixture was measured at 30 minute 25 intervals until a value of 5 or less was obtained. A small volume of diethylene glycol was added if the acid number was greater than 5 and did not change between successive samplings.

When the acid number of the reaction mixture measured 5 or less, heating of the reaction mixture was discontinued and the mixture allowed to cool to 90° C. At this time a volume of a 10 weight percent aqueous potassium hydroxide solution equal to about 1/3 the volume of the reaction mixture was added to the reactor. After about 15 minutes of stirring the aqueous

5 layer was separated and discarded. The organic layer was washed three times using volumes of 10 weight percent aqueous potassium hydroxide solution equal to that used for the first washing, followed by at least three washings with hot deionized water until the pH of the organic layer was 7.

10 The types and relative concentrations of esters in the reaction product, a clear, colorless liquid, was determined using a Hewlett Packard HP6890 series gas chromatograph equipped with a type HP-5 column packed with phenyldimethylpolysiloxane that was 5% crosslinked. The column temperature was gradually increased from 80 to 320° C and the rate of helium flow was 200 cc. per minute.

15 The chromatogram generated by passage of an ester mixture through the detector of the gas chromatograph contained four or five peaks, each corresponding to one of the component esters. The area under a given peak was considered directly proportional to the relative concentration of the corresponding ester. Under the operating conditions of the 20 chromatograph the esters emerged in the following order: the monobenzoate of diethylene glycol (DEGMB), the monolaurate (DEGML), the dibenzoate (DEGDB), the mixed benzoate/laurate (DEGBL) and the dilaurate (DEGDL).

The molar ratio of benzoic acid to lauric acid used for each of the four esterification reactions 25 is recorded in Table I, together with the percent of total peak area on the chromatogram corresponding to each of the aforementioned five possible products. In each of the initial reaction mixtures the molar ratio of diethylene glycol to total carboxylic acids was 1: 2.

TABLE 1

Benzoic Acid : Lauric Acid Mole Ratio ¹	% DEGMB ²	% DEGML	% DEGDB	% DEGBL	% DEGDL
1:1 (DEGBL)	<0.5	4	14	45	36
3:1 (DEG3BL)	<0.5	<1	38	46	15
6:1 (DEG6BL)	<0.5	<2	58	30	9
9:1 (DEG9BL)	<0.5	<1	72	22	4
12:1 (DEG12BL)	<0.5	<1	77	19	2

1 = All mole ratios refer to reactants

5 2 = All percentages based on total reaction product

Example 2

This example demonstrates the relatively low freezing point, viscosity and volatility that

make the present ester mixtures desirable plasticizers for polyvinyl chloride and other rigid

10 organic polymers.

The freezing points of the esters mixtures described in Example 1 that were liquid at ambient

temperature were determined by exposing the ester mixtures to a mixture of ethylene glycol

and water that was cooled to the desired temperature using a refrigeration unit. The

15 temperature of the mixture containing a sample of the ester to be evaluated was initially

25° C and was lowered in increments of 5° C. Each temperature level was maintained for 24

hours. The sample was examined at the end of each 24-hour period to determine if the

initially liquid ester composition had solidified. The temperature at which solid material was

first observed was reported as the freezing point of the ester mixture being evaluated and is

20 recorded in Table 2. For comparative purposes, pure diethylene glycol dibenzoate freezes at

25°C.

The viscosities of the esters were measured at 25° C using a stress-controlled rheometer

manufactured by TA Instruments and equipped with a 4 cm-diameter cone-shaped plate.

25 The esters are identified in the same manner as in the preceding Table 1.

TABLE 2

	BENZOIC ACID/ LAURIC ACID MOLE RATIO	FREEZING TEMP.(° C.)	VISCOSITY @ 5° C. ¹
5	1:1 (DEGBL)	25	(Solid)
	3:1 (DEG3BL)	5	0.13
	6:1 (DEG6BL)	-5	0.15
	9:1 (DEG9BL)	-15	0.18
	12:1 (DEG12BL)	-10	0.28
	DEGDB ²	25	0.43 (supercooled)
15	1 = Viscosity in Pascal Seconds (Pa.s) 2 = Diethylene glycol dibenzoate (evaluated for comparative purposes and known to supercool)		

The volatility of the esters was determined using a model TGA2950 thermogravimetric analyzer manufactured by TA Instruments. The percentage weight change was measured by exposing the sample to a temperature of 190°C for 3 hours under a flow of nitrogen at a rate of 100 cc. per minute. The percent weight loss of each ester was determined at 30 minute intervals and the results are recorded in Table 3. Di-2-ethylhexyl phthalate (DOP) was evaluated for comparative purposes.

25

Table 3

Time (Min.)	% Weight Loss					
	DEGBL	DEG3BL	DEG6BL	DEG9BL	DEGDB	DOP*
0	0	0	0	0	0	0
30	9.8	11.4	14.5	11.2	28.7	18.1
60	20.6	23.3	28.0	23.1	53.0	37.1
90	29.8	32.6	37.2	33.5	71.0	56.1
120	37.8	41.1	47.1	42.9	83.4	76.0
150	44.7	48.7	58.0	51.0	92.1	90.4
180	50.7	55.4	64.5	60.0	100	95.7

* = Dioctyl Phthalate (Comparison)

30

The data in Tables 2 and 3 demonstrate the unexpectedly lower volatility of DEG9BL relative to DEG6BL, which, in turn, exhibited higher values than DEG3BL. This is an unexpected

reversal of the observed trend toward higher values of viscosity and volatility with increasing benzoic acid content.

Example 3

- 5 This example demonstrates the utility of the mixed esters of this invention as plasticizers for polyvinyl chloride (PVC) compositions. Preferred esters of the present invention exhibit a unique combination of high solvating ability for the polymer with a relatively low viscosity of the plasticized polymer composition.
- 10 The ester compositions were incorporated into two plastisol formulations. The plasticizer was used at levels of 30 and 55 parts by weight per 100 parts of PVC resin(s).

The types and amounts of ingredients in the two formulations evaluated are recorded in Table 4.

15

TABLE 4

	Formulation A	B
Ingredient	Parts	Parts
PVC	100	60
Blending Resin	0	40
Plasticizer	55	30
TXIB ¹	3	6
ESO ²	4	4
Stabilizer ³	3	3

1 = Texanol® isobutyrate

2 = Epoxidized Soybean Oil

20 3 = A calcium/zinc stabilizer available as Irgastab CZ 116 from Witco Chemical Corporation

The polyvinyl chloride was prepared by microsuspension polymerization and exhibited a weight average molecular weight of 200,000. It is available as Lacovyl PB 1302 from Atochem.

- 5 The blending resin was a vinyl chloride homopolymer prepared by suspension polymerization, exhibited a weight average molecular weight of 140,000, and is available as Vinnolit C65V from Wacker Chemie. The purpose of the blending resin was to reduce the viscosity of the plastisol.
- 10 Both of these polymers were in the form of finely divided solids.

Plastisols were prepared by first blending the liquid ingredients using a high speed mixer. The resultant mixture was cooled using an ice/water bath to prevent gelation of the composition during addition of the vinyl chloride polymer(s). Following addition of the polymer(s) the 15 composition was stirred at a mixer speed of 1200 revolutions per minute for 10 minutes then deaerated for 30 minutes under reduced pressure with stirring.

The viscosity of the resultant deaerated plastisols A and B were measured using a stress-controlled rheometer manufactured by TA Instruments. The spindle of the instrument was 20 equipped with a plate measuring 2 cm. in diameter. The shear rate was 10 sec.⁻¹ under ambient conditions.

The gelation temperatures of the plastisols were determined using the same rheometer and 2 cm.-diameter plate used to determine viscosity. In this instance the plate was oscillated rather than rotated as in the case of the viscosity measurement. The temperature of the metal block 25 on which the sample of plastisol rested was gradually increased until gelation of the plasticizer occurred, which was evidenced by a sudden increase in the torque required to oscillate the plate.

When changing the plasticizer in a plastisol results in a lowering of the gelation temperature, this is associated with greater solvating ability of the plasticizer. The viscosity and gelation temperature of the plastiols evaluated are recorded in Table 4.

5

Plastiols corresponding to formulations A and B but using di2-ethylhexyl phthalate or a 1:1 weight ratio mixture of diethylene glycol dibenzoate and triethylene glycol dibenzoate in place of a mixed ester composition of the present invention were prepared and evaluated for comparative purposes.

10

The viscosity and gelation temperature of the plastiols are recorded in Table 4.

Table 4

Plasticizer	Viscosity (Pa·s)	Gelation Temperature (°C)
DEG3BL	1.1	67
DEG6BL	1.5	65
DEG9BL	1.6	65
DEGDB/ TEGDB ¹	3.5	63
DOP	1.8	76

- 15 1) a 1:1 weight ratio mixture of diethylene glycol dibenzoate and triethylene glycol dibenzoate used for comparative purposes

The data in Table 4 demonstrate the unique combination of low viscosity and increased solvating ability, as evidenced by a lower gelation temperature, that distinguish preferred 20 embodiments of the present mixed esters relative to widely used plasticizers for vinyl chloride polymers.

Example 4

This example demonstrates the compatibility of the present ester mixtures with polyvinyl chloride.

- 5 The plastisols to be evaluated were coated on release paper and fused by heating at 200°C for 2 minutes. The resultant sheets were about 1 mm. thick. Samples measuring 1 x 3 inches (2.54 x 7.62 cm.) were cut from the sheets. The samples were then removed from the paper backing and folded to form a U-shaped loop, compressed within a binder clip, heated and then evaluated in accordance with the procedure described in ASTM test D 3291-92. The test
10 samples were heated at 73° C for 24 hours. Following heating the curved interior portion of each sample was daubed with a cigarette paper to determine whether any plasticizer had exuded from the polymer. The amount of exuded liquid was rated on a scale of from 0 (no liquid present), to 3 (surfaces of polymer and paper covered with continuous films of liquid exudate). All of the test samples evaluated were rated “0” with the exception of the sample
15 containing 55 parts by weight of the mixed ester referred to in Table I as DEG3BL. This sample was given a rating of “1”, indicating only slight exudation with faint, discontinuous marks on the paper.

THAT WHICH IS CLAIMED IS :**1. An ester composition comprising****1) an ester corresponding to formula (I)****2) an ester corresponding to formula (II)****3) an ester corresponding to formula (III)**

wherein R^1 is at least one radical selected from the group consisting of phenyl and alkyl-substituted phenyl, R^2 is a divalent radical of the formula $-\text{R}^4(\text{OR}^4)_m-$, R^3 is an alkyl radical containing from 3 to 21 carbon atoms, R^4 is an alkyl radical containing from 2 to 4 carbon atoms, and m represents 0 or the integer 1 or 2.

2. A composition according to claim 1 wherein the molar ratio of $\text{R}^1\text{C(O)}$ - to $\text{R}^3\text{C(O)}$ - groups in said composition is at least 1: 1 and said composition is a liquid at 25° C.**3. A composition according to claim 2 wherein said molar ratio is from 1:1 to 12:1.****4. A composition according to claim 3 wherein said composition additionally contains at least one ester exhibiting a formula selected from the group consisting of $\text{R}^1\text{C(O)OR}^2\text{OH}$ and $\text{R}^3\text{C(O)OR}^2\text{OH}$.****5. A composition according to claim 1 wherein R^1 is phenyl, m is 1 or 2 and R^3 contains from 8 to 16 carbon atoms.****6. A composition according to claim 5 wherein R^4 is ethyl or propyl and R^3 contains 11 carbon atoms.**

7. A plasticized polymer composition comprising 1) a polymer selected from the group consisting of homopolymers and copolymers of vinyl chloride and 2) a plasticizer comprising

1) an ester corresponding to formula (I)



2) an ester corresponding to formula (II)



3) an ester corresponding to formula (III)



wherein R^1 is at least one radical selected from the group consisting of phenyl and alkyl-substituted phenyl, R^2 is a divalent radical of the formula $-\text{R}^4(\text{OR}^4)_m-$, R^3 is an alkyl radical containing from 3 to 21 carbon atoms, R^4 is an alkyl radical containing from 2 to 4 carbon atoms, and m represents 0 or the integer 1 or 2.

8. A polymer composition according to claim 7 wherein the molar ratio of $\text{R}^1\text{C(O)-}$ to $\text{R}^3\text{C(O)-}$ groups in said composition is at least 1: 1, and said composition is a liquid at 25° C.

9. A polymer composition according to claim 8 wherein said molar ratio is from 1:1 to 12:1.

10. A polymer composition according to claim 7 wherein R^1 is phenyl and m is 1 or 2 and R^3 contains from 8 to 16 carbon atoms.

11. A polymer composition according to claim 10 wherein R^4 is ethyl or propyl and R^3 contains 11 carbon atoms.

A. CLASSIFICATION OF SUBJECT MATTER				
IPC 7	C07C69/76	C07C69/78	C08K5/103	C08L27/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C C08K C07K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 585 448 A (EMERSON WILLIAM S ET AL) 12 February 1952 (1952-02-12) column 1, line 30 -column 2, line 20; claims; examples ---	1-11
A	GB 715 995 A (MONSANTO CHEMICALS) 22 September 1954 (1954-09-22) page 1, line 49 -page 2, line 58; claims; example ---	1-11
A	WO 01 00722 A (SJOEGREEN CARL AXEL ;OGEMARK KEITH (SE); PERSTORP AB (SE)) 4 January 2001 (2001-01-04) claims; examples 1,2 ---	1-11
A	US 3 370 032 A (POTTER GEORGE H) 20 February 1968 (1968-02-20) claims; examples -----	1-11

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

12 July 2002

Date of mailing of the international search report

18/07/2002

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